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# TECHNICAL NOTE

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OXIDATION BEHAVIOR OF BINARY NIOBIUM ALLOYS

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SUMMARY

This investigation concludes a study to determine the effects of up to 25 atomic percent of 33 alloying additions on the oxidation characteristics of niobium. The alloys were evaluated by oxidizing in an air atmosphere for 4 hours at 1000° C and 2 hours at 1200° C.

Titanium and chromium improved oxidation resistance at both evaluation conditions. Vanadium and aluminum improved oxidation resistance at 1000° C, even though the V scale tended to liquefy and the Al specimens became brittle and the scale powdery. Copper, cobalt, iron, and iridium improved oxidation resistance at 1200° C. Other investigations report tungsten and molybdenum are protective up to about 1000° C, and tantalum at 1100° C.

The most important factor influencing the rate of oxidation was the ion size of the alloy additions. Ions slightly smaller than the  $Nb^{+5}$  ion are soluble in the oxide lattice and tend to lower the compressive stresses in the bulk scale that lead to cracking. The solubility of the alloying addition also depends on the valence to some extent. All of the elements mentioned that improve the oxidation resistance of Nb fit this size criterion with the possible exception of Al, whose extremely small size in large concentrations would probably lead to the formation of a powdery scale. Maintenance of a crack-free bulk scale for as long as possible may contribute to the formation of a dark subscale that ultimately is rate-controlling in the oxidation process.

The platinum-group metals, especially Ir, appear to protect by entrapment of the finely dispersed alloying element by the incoming  $Nb_2O_5$  metal-oxide interface. This inert metallic Ir when alloyed in a sufficient amount with Nb appears to give a ductile phase dispersed in the brittle oxide. This scale would then flow more easily to relieve the large compressive stresses to delay cracking. Complex oxide formation (which both Ti and Zr tend to initiate) and valence effects, which probably change the vacancy concentration in the scale, are masked by the overriding tendency for a porous scale.

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## INTRODUCTION

Pure niobium has outstanding strength in the temperature range of 1000° to 1200° C, good ductility at room and elevated temperatures, and a low capture cross section for thermal neutrons. Despite these desirable characteristics, its widespread use in aircraft, missiles, and certain reactors is limited because it lacks oxidation resistance. There are two methods by which the oxidation resistance can be increased. The first is by coating with an oxidation-resistant layer. This method has been extensively studied (ref. 1) with only moderate success. A second method of improving oxidation resistance is through alloying. This approach is more advantageous in that the scale that provides protection is regenerative. This latter method was studied in this investigation.

Published research has shown that the scale formed on niobium above about 600° C is porous and nonprotective; therefore, the first goal of the alloying addition is to provide a scale that is tight and adherent, and whose rate of growth is diffusion-controlled. The rate of growth of this scale may then be further improved by additional alloying.

This is the second and concluding report of an investigation conducted as a qualitative screening study to indicate promising binary alloys that provide adherent scales and would therefore warrant further study. From the results of these studies, possible mechanisms of oxidation are suggested. The first report (ref. 2) contained data on the oxidation characteristics at 1000° C for 4 hours and 1200° C for 2 hours of binary alloys of niobium containing up to approximately 25 atomic percent aluminum, silicon, titanium, vanadium, chromium, iron, cobalt, nickel, copper, germanium, selenium, zirconium, molybdenum, tantalum, tungsten, rhenium, or iridium. Of these, titanium and chromium gave the best protection. It was noted that elements that conferred protection had an ion size close to that of the  $\text{Nb}^{+5}$  ion and generally a lower valance.

This report extends the screening data to binary alloys of niobium containing up to nominally 25 atomic percent boron, calcium, scandium, manganese, ruthenium, rhodium, palladium, tin, antimony, praseodymium, neodymium, hafnium, osmium, platinum, lead, or thorium. Thus, the two reports cover a total of 33 systems. In the first report (ref. 2) alloying elements were selected that were believed to alloy readily with niobium or that were known to confer oxidation resistance in other systems. In addition to this basis of selection, for the study described herein elements were selected to confirm the size and valence effects described previously (Hf, Th); to include a more complete coverage of the periodic table (Sc, Mn, Pr, Nd); to investigate further groups where previous results were ambiguous or a random promising value was obtained (Ru, Rh, Pd); and to include elements that met previous selection standards but were eliminated because they were low melting (Sn, Pb). It was recognized

that many of the elements tried were not of value to produce practical alloys, but it was felt they might shed some light on the mechanism involved. An attempt was also made to produce alloys of magnesium, zinc, and silver, but these alloying elements could not be retained during processing because of their high vapor pressure at the temperatures where attempts to sinter these alloy systems were made. When the sintering temperature was reduced to a point where the loss was not excessive, virtually no alloying with niobium took place. These elements thus could not be tested.

As in the initial study, the specimens were 1/2-inch-diameter by 1/8-inch-thick disks prepared by powder-metallurgy techniques. Evaluations were conducted for 4 hours at 1000° C and 2 hours at 1200° C in a horizontal tube furnace. Both the changes in weight of the alloys and the physical character of the scales were noted.

This report also compares the results obtained in this study with (1) those reported in reference 2, (2) additional compositions reported in the literature, and (3) some compositions, similar to those reported herein, but produced by the authors using nonconsumable electrode-arc button melting.

## MATERIALS, APPARATUS, AND PROCEDURE

### Materials

Niobium of 99+ percent purity, obtained from Fansteel Metallurgical Corp. was used in the initial study of niobium binary alloys (ref. 2). Because of the unavailability of the required quantities of this powder, the oxidation characteristics of specimens made from various sizes of powders supplied by Hermann C. Starck, Murex Ltd., and Kennametal, Inc., were determined, and the results were compared with those previously obtained with Fansteel niobium. No difference in oxidation characteristics could be detected. Starck niobium of -325 mesh, 99+ percent purity was selected for this study.

The sources, particle sizes, and composition of the alloying elements, provided by the supplier, are shown in table I arranged in order of increasing atomic number.

### Specimen Fabrication

The procedure used to fabricate the specimens was identical to that described in reference 2, and is briefly summarized as follows:

(1) Batches of approximately 10 grams of niobium and 1, 2, 5, 10, and 25 atomic percent of the alloying additions were ground in a hand mortar and thoroughly mixed by mechanically tumbling in glass vials.

(2) Disks weighing 2 grams and approximately  $1/8$  inch thick by  $1/2$ -inch diameter were cold-pressed in steel dies at a pressure of 100,000 pounds per square inch. No lubricant was used.

(3) In most cases the disks were given an initial sinter in a vacuum of 5 microns of mercury or less at the temperatures indicated in table II. Where the vapor pressure of the alloying addition was high, a slight amount of argon was back-filled and used as the sintering atmosphere. The argon atmosphere was purified by passing it through a cold trap containing a low-molecular-weight hydrocarbon and dry ice at  $-40^{\circ}\text{C}$  and through a column containing titanium chips at  $800^{\circ}\text{C}$ . Where the melting point of the alloying addition was low, the sintering temperature was reduced to a point where the alloy would not fuse. In these cases exploratory sinters were used to determine the final conditions. In several cases less than five compositions were studied; this was done where a low-melting-point eutectic was formed (i.e., Fe, Ni) or the specimens were extremely brittle (Pr, Nd).

(4) After sintering, the disks were re-pressed at 150,000 pounds per square inch and resintered at the temperatures indicated in table II.

(5) The final compositions of the disks were estimated from a chemical analysis of the nominally 25-atomic-percent alloy of each binary combination. Where large discrepancies between the measured and nominal compositions were found, the lower compositions were also analyzed. These are shown in figure 1. No chemical analyses are available for the Ca alloys, since the specimens disintegrated because of oxygen pickup before the analyses could be made.

(6) Before oxidation testing, the specimens were polished with 3/0 emery paper, cleaned in acetone, and weighed. The specific fabrication conditions for each system are shown in table II.

#### Evaluation Procedure

The specimens were oxidized in an Alundum boat in a tube furnace. Two evaluation conditions were used:  $1000^{\circ}\text{C}$  for 4 hours and  $1200^{\circ}\text{C}$  for 2 hours. Air that had been dried to a dewpoint of approximately  $-51^{\circ}\text{C}$  by passing through a column of desiccant was circulated through the 2-inch furnace at a muffle rate of approximately 2 cubic feet per hour.

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After oxidation, the specimens together with spalled fragments of the scale were reweighed, and the general appearance of both the remaining alloy disk and the scale was noted. In some cases the extensive spalling of the scales made changes in weight difficult to obtain. In spite of this, it is believed that the changes in weight were determined with sufficient accuracy for screening purposes. From its appearance, each scale was classified by assigning a number ranging from 1 for tight adherent scales to 5 for voluminous porous scales. Typical examples of each scale rating are shown in figure 2. Where the scales were of a promising type or where weight-gain data were misleading, the scales were further classified as V, L, P, or S, which are defined as follows:

- V    The scale appeared to have volatilized. This rating was assigned when the volume of scale appeared small for the volume of metal that remained.
- L    The scale appeared to have been liquid at the testing temperature.
- P    The scale had a powdery texture.
- S    The scale was type 1 or 2 but spalled upon cooling.

In those cases where the color of the scale was unusual or where a class 1 scale was encountered, the scale was studied by X-ray diffraction and chemical analysis. The X-ray patterns were made with a Norelco 50-kilovolt unit and Geiger-counter diffractometer. Pieces of scale that had spalled or were carefully removed by scraping were ground in a mortar and then sprinkled into the powder sample holder. A glancing X-ray pattern was taken.

## RESULTS

### Comments Regarding Experimental Materials

It is recognized that the fabrication conditions were not optimum for each composition. In many cases, no information on which to base fabrication conditions was available in the literature; hence, optimizing the fabrication conditions for each composition would require a major research effort. This necessarily would have cut down on the number of systems that could be studied. The conditions used are believed to be adequate to reveal those elements that are superior in providing oxidation resistance and that should be studied in greater detail. The fact that most binary combinations were studied with five compositions should further reduce the probability that lack of the best fabrication conditions resulted in overlooking a promising alloy. As was indicated previously, sintering times longer than 1/2 hour were not considered necessary above

3000° F (ref. 2). There was some question whether a 3500° F sinter for 1/2 hour was sufficient to thoroughly alloy high-melting-point elements like tungsten and molybdenum with niobium. However, d-values obtained from X-ray analyses of selected solid-solution alloy specimens showed only very slight deviation from Vegard's Law.

The chemical compositions of the specimens are shown in figure 1. As expected, many alloys showed appreciable loss of the alloying additions during sintering, comparable to the loss of chromium, aluminum, and titanium in alloys reported previously (ref. 2). This was due to the high volatility of the alloying elements at the high sintering temperature required. In a few cases (i.e., W and Ir), the niobium vaporized in preference to the less volatile alloying element.

Density measurements of the sintered compact were made by several methods. These included the Archimedes displacement technique with and without oil impregnation, precision measurement of the samples, and pore measurement from the photomicrographs. These various methods did not give results in good agreement. The specimens ranged from about 70 to 90 percent dense depending on the alloying elements. In general, the alloys that approached 90 percent density were in those binary systems that showed good solubility of the alloying element with niobium.

The kinetics of oxidation of a sintered niobium-titanium alloy were compared with those of an arc-melted alloy of the same composition. The more porous sintered alloy scaled at only a slightly higher rate. On this basis it was concluded that the scaling rates obtained with the relatively porous specimen used in this study would be valid for comparing the effects of different alloying elements. The shapes of the curves for the sintered and arc-cast specimens were similar, indicating that the porous sample probably had a greater true area.

Figure 3 shows the microstructures of two typical alloys. The niobium - 2 percent vanadium alloy represents a single-phase alloy, while the niobium - 1 percent cobalt alloy represents a two-phase alloy. These photomicrographs were typical of the specimens studied.

Studies of oxygen penetration into the metal during oxidation were not made, because both chemical analyses and some microhardness traverses showed that the alloy were nearly saturated with oxygen before test. This is due to the use of fine-mesh niobium powder, which contains appreciable chemisorbed oxygen. While it is appreciated that oxygen penetration is very important with respect to both oxidation and mechanical properties, it was not practical to study this effect in so many alloy systems, where sintering conditions could not be closely controlled. As will be discussed later, the dissolved oxygen in the niobium alloy matrix did not alter the overall gross scaling effects of the various binary systems.



## Comparison of Effects of Various Alloying Elements on Oxidation Behavior

The results of this and the previous (ref. 2) screening study are represented as individual bars placed on a periodic table in figure 1. An explanatory key is provided in the upper right corner of the figure. The rate is given as  $\text{mg}/(\text{sq cm})(\text{hr})$  and is assumed to be linear. For comparison purposes a horizontal line giving the weight gain of unalloyed niobium is included in each group of bars on the figure. This value was obtained from unalloyed niobium specimens included with the evaluation of each system. A considerable scatter in the values for unalloyed niobium can be noted, especially for unalloyed specimens scaled with alloys of poorer oxidation resistance. The exact reason for this variation is not known, but it appears that it is caused by difference in density of the unalloyed niobium specimens (they were fabricated using the conditions for the specific binary system with which they were evaluated), or possibly by surface pickup of the alloying elements from adjacent test specimens, as indicated by a difference in color for these unalloyed specimens when compared with niobium oxidized alone.

It is evident from figure 1 that none of the alloying elements covered by the second phase of this screening study conferred outstanding oxidation resistance to niobium. However, they did aid in understanding the nature of the formation of protective scales on niobium alloys, as will be discussed later. In further discussion, no distinction will be made between the alloying additives covered by reference 1 and this study.

The results in figure 1 indicate that titanium, chromium, aluminum, and vanadium are the most promising additions at  $1000^{\circ}$  and  $1200^{\circ}$  C (ref. 2), although not equally so at both temperatures. They reduce the rate of oxidation. A more detailed study of the niobium-chromium system has shown that, at  $1200^{\circ}$  C, chromium is of little benefit (ref. 3). Titanium, chromium, and vanadium have the further advantage of not excessively depressing the melting point of niobium. Other elements (still from ref. 2) offer fair protection under certain conditions. Aluminum and vanadium additions produce class 1 scales at  $1000^{\circ}$  C with poorer scales at  $1200^{\circ}$  C. In contrast, rhenium-, cobalt-, copper-, and iridium-containing alloys have better scales at  $1200^{\circ}$  than at  $1000^{\circ}$  C. However, rhenium oxide volatilizes, and many of the other alloys containing cobalt, copper, and iridium are brittle because of the many intermetallic compounds they form with niobium. The 5-atomic-percent (nominal) alloy of iron improves from a class 2 scale at  $1000^{\circ}$  C to a class 1 scale at  $1200^{\circ}$  C. Silicon, zirconium, tantalum, and molybdenum have some, but less, promise.

### Comparison of Results with Those Reported in Literature

The considerable potential of niobium has resulted in numerous investigations of methods of reducing its rate of oxidation. Since the standard criteria were used by each investigator for selection of many of the elements for inhibiting oxidation, it is natural that these programs should include many of the same alloying additions. This overlap is informative because it affords each laboratory a basis of comparison and also because it enables a comparison of the effectiveness of various processing techniques.

Summaries of the data from the literature as well as this study are given in the last column of table III.

It is interesting to compare the results reported herein with those in the literature. Reference 4 reports that tantalum conferred protection in arc-melted niobium buttons at 20 atomic percent at close to  $1100^{\circ}\text{C}$ , but the data obtained in this investigation and those reported in reference 5 for tantalum do not confirm this. The weight gains resulting from additions of vanadium and molybdenum are low in this study as well as in other studies (refs. 4 to 6). Tungsten was not found as protective in this investigation as in reference 5.

### Composition of Scale

The chemical analyses and colors of the scales that were promising are given in table IV, and their  $d$ -values (as determined by X-ray diffraction) are given in tables V and VI. On the basis of the chemical analyses, color changes, and  $d$ -values, it is apparent that many alloying additions were dissolved in the  $\text{Nb}_2\text{O}_5$ . These scales were of the same  $\text{H}\cdot\text{Nb}_2\text{O}_5$  type that is found on unalloyed niobium at these temperatures.

## DISCUSSION OF CONCEPTS INVOLVED IN OXIDATION OF BINARY NIOBIUM ALLOYS

### Criteria for Alloy Additions

There are several approaches for enhancing the oxidation resistance of a metal by alloying additions. First, however, the alloying addition must have enough solubility in niobium that it can affect the oxidation reaction. It would, of course, be desirable that the alloy not adversely affect the fabricability and strength. This alloying characteristic is shown in the third column of table III. In general, elements with high solubility have the best chance of altering the oxidation character without harming the mechanical properties of the alloy. The fourth column indicates whether an addition element might form a preferential scale based

on a comparison of its free energy of formation with that of  $\text{Nb}_2\text{O}_5$  (per mole of oxygen). This preferential scale can form if enough of the alloying addition is present in the matrix. On the basis of calculations, so much alloying addition would be required in some cases (e.g., Nb-Zr system) to form a preferential scale that it is unlikely that the alloy would have the desirable strength characteristics of niobium. In the ranges of composition within which alloys have been studied, a pure preferential scale is not formed. Instead, the scales contain enough niobium ions that they can be termed niobates.

An aid in selecting alloying additions is to understand the effects of these additions on the oxidation characteristics of other alloy systems. Where this information is not available, it is helpful to know the scaling behavior of the pure alloying element. Usually an element that forms a tight, adherent, diffusion-controlled scale is preferred. Column 5 in table III shows which are ordinarily the best additions for oxidation resistance. These are aluminum, silicon, and chromium. Manganese, iron, cobalt, nickel, and copper also have a diffusion-controlled scale, but the diffusion rates of the ions are rather high. This scale, if imparted to niobium, might be the first step toward protection. For niobium as well as other poor oxidation-resistant metals, the most important criteria are found in column 6. Niobium scales catastrophically because it forms a porous oxide caused by the large compressible stresses generated in the growing  $\text{Nb}_2\text{O}_5$ . It becomes necessary to lower this compressive stress by dissolving smaller ions in place of the  $\text{Nb}^{+5}$  ion. If the smaller ions can lower the volume ratio of this oxide to where it does not fracture, a diffusion-controlled scale is formed. Then diffusion rates of the scale can be further altered by small additions of ions of various valences depending on the electrical nature of the scale formed.

#### Subscale Formation

There appears to be some ambiguity concerning the presence of subscales during the oxidation of niobium and its alloys. Several references (refs. 7 and 8) agree that pure niobium forms a single-layer scale, while others (ref. 9) report the presence of a thin black subscale found either adjacent to the metal or on the underside of the spalled scale. Since there is a good likelihood that this subscale if formed would control the overall rate of oxidation of niobium alloys, its presence was carefully sought in the systems that appeared promising by taking glancing diffraction patterns of the metal surface after stripping the scale and of the underside of the scale itself. In none of these was it detected. Despite the absence of the subscale (as stated previously where literature comparisons could be made), results were comparable.

In a separate series of nonconsumable electrode-arc-melted niobium-titanium alloy buttons, however, a thin black underlayer was noted after

oxidation. It was found in increased amounts with increasing titanium content after scaling in air for approximately 24 hours in runs up to 1200° C. It gave a somewhat lower scaling rate (about two-thirds after 8 hr) than powder-metallurgy buttons of the same composition. This subscale could not be positively identified; however, it is likely to be a lower oxide of niobium. As such, its oxide to metal volume ratio will be somewhat lower than the rather high 2.54 to 2.68 Pilling-Bedworth (P-B) ratio calculated for Nb<sub>2</sub>O<sub>5</sub> and would tend to stabilize the Nb<sub>2</sub>O<sub>5</sub> (refs. 6 and 10) by lowering the compressive stress in the scale. It is probably this compressive stress that tends to crack the scale and render it porous in the case of pure niobium. This subscale forms to a greater degree under a low partial pressure of oxygen (ref. 5). It was not found in this investigation on the relatively porous sintered niobium or niobium alloy specimens. Apparently the entrapped oxygen in the pores of the powder-metallurgy specimens as well as the large dissolved oxygen content of the niobium itself resulted in a greater partial pressure of oxygen and was sufficient to forestall the formation of this subscale.

#### Effect of Alloying Elements on Subscale and Resultant Kinetics

Niobium probably starts to scale parabolically and dissolves oxygen in its matrix at the same time. Usually in unalloyed niobium a breakaway (change from a parabolic rate) occurs because of the large volume ratio of the oxide to metal. The time for the breakaway is a function of several factors. In the case of unalloyed niobium, probably the principal factor affecting the time for breakaway is the oxygen in the pores, on the surface, and dissolved in the niobium. In the case of niobium alloys, these factors are further affected by an altered P-B ratio of the scale. When smaller ions dissolve in the oxide lattice (such as Ti and Cr), this volume ratio is reduced, and the scale will grow to greater thickness before it tends to crack. While the Nb<sub>2</sub>O<sub>5</sub> is growing by anion (oxygen) diffusion (ref. 11), there is a concentration gradient of oxygen across the scale, resulting, if the gradient is large enough, in a lower oxide adjacent to the matrix. This lower oxide appears more coherent with the matrix than the Nb<sub>2</sub>O<sub>5</sub> and seems to approach a protective scale (ref. 9). This inner scale then becomes rate-controlling, and its concentration gradient determines the scaling rate. Meanwhile, the outer Nb<sub>2</sub>O<sub>5</sub> scale reaches a critical thickness that depends on such factors as temperature, geometry, water-vapor content of the air, plasticity imparted by the alloying elements, and the degree of lattice matching between the lower oxide and the matrix. Finally, the Nb<sub>2</sub>O<sub>5</sub> cracks and becomes porous, resulting in the breakaway to a linear rate (refs. 7 and 11). This linear rate could be of various types. First, the scale

could crack sufficiently to render both the outer and inner scale porous so that metal would oxidize directly in a catastrophic manner. Secondly, the outer scale could crack and the inner scale could remain intact, but enough oxygen would reach the inner scale to oxidize it to a higher oxide, keeping the inner layer a constant thickness and giving a linear but non-catastrophic rate. Possible combinations of the preceding can be imagined, so that almost any rate curve and scale characteristics between these limits might be expected.

### Preferential Oxide Formation

The free energies of formation of the oxides of several of the alloying additions (Ti, Zr, and Th) were lower than that for  $\text{Nb}_2\text{O}_5$ . Such elements are indicated by the word "yes" in column 4 of table III. These elements, if alloyed in adequate concentration, might form preferential scales that are protective. While no such scales were found, the greater concentration of the alloying element in the scale than in the bulk alloy (table IV) for titanium and zirconium indicates some tendency in this direction.

There are data showing that titanium at high concentrations tends to form  $\text{TiO}_2$  preferentially or at least a titanium niobate (ref. 12). Zirconium also at higher concentrations appear to protect by means of the preferential formation of zirconia or a complex oxide ( $6\text{ZrO}_2 \cdot \text{Nb}_2\text{O}_5$ ) (ref. 11). It is interesting to note that, at low zirconium concentrations where only  $\text{Nb}_2\text{O}_5$  is formed, the oxidation rate of niobium is increased (ref. 5).

The greatest concentrations of alloying elements in the scales analyzed were with 25 percent tantalum at  $1000^\circ\text{C}$  and 25 percent iridium at  $1200^\circ\text{C}$ . Indications from X-ray data (table VI) are that the iridium is present in the oxide as a finely dispersed metallic second phase (since it has d-values the same as pure Ir). Attempts to confirm this by chemical analyses were inconclusive. It seems when enough is present in the  $\text{Nb}_2\text{O}_5$  it gives the type 1 scale that appears protective. The other platinum-group metals show this same tendency, though not to the extent of iridium. If true, this would offer a unique method of protecting metals that form oxides of very high volume ratios - namely, dispersing a finely divided inert platinum-group metal in the oxide. This would also increase the plasticity of the scale.

Despite these examples, the fact that only  $\text{H} \cdot \text{Nb}_2\text{O}_5$  was found in most protective scales indicates that the tendency for preferential oxide formation does not appear to be an important mechanism for protecting niobium at low alloy compositions.

In this and other investigations, elements or representatives of groups of elements that might form a preferential oxide or binary alloys of niobium when scaled at high temperatures were examined. In this group of 14 elements only two (Ti and Al) conferred any degree of protection at low alloy concentrations. Furthermore, this mode of protection does not show much promise for future alloy development, since roughly half the elements that increased protection did not have favorable energies of oxide formation (table III). Many of those elements that did (Th, Nd) had very limited solubility in niobium. Perhaps the limits of solubility of these elements in the alloy could be increased by the presence of additional elements.

#### Diffusion Effects in Scale

Another method of oxidation protection is that proposed by Wagner for diffusion-controlled (nonporous) oxides (ref. 10). His theory states that, when elements of either a higher or lower valence than that of the matrix metal are dissolved in dilute amounts in a matrix oxide, the ion transfer rates are changed, thereby giving a change in scaling rate if ion transfer is rate-controlling. In the case of  $\text{Nb}_2\text{O}_5$ , which is an anion-deficient, anion-diffusion-controlled oxide (refs. 6, 9, and 10), higher-valence solute cations would be expected to lower the scaling rate. In the case of a tendency to form a porous scale as niobium does, this mechanism would only operate before the breakaway to a linear rate in the bulk oxide. Its only effect would be to prolong the time to breakaway, since a critical thickness for cracking of the scale based on the volume ratio of  $\text{Nb}_2\text{O}_5$  to metal should not change appreciably. By doing so it would allow the subscale to grow for a longer time, and, by slowing down oxygen diffusion, possibly to produce a greater thickness. The greater the thickness of this subscale, the greater the ultimate protection. Alloying additions of tungsten, molybdenum, and rhenium would be expected to protect in this manner. There is some indication that they do, especially molybdenum and tungsten (see table VI), but any localized formation of the oxide of the alloying element tends to lead to volatilization of the scale, since it takes on the character of the oxide of the alloying element.

The Wagner valence effect might have a more important effect on the diffusion rates in the subscale. Since the subscale is more easily formed at a reduced oxygen pressure, the Wagner valence effect in niobium could more easily be studied under controlled pressures. Another similar approach would be to plug the anion holes in the  $\text{Nb}_2\text{O}_5$  with an anion-like fluorine which, since it has a lower valence, should also lower the anion diffusion rate in  $\text{Nb}_2\text{O}_5$ . It is also a slightly smaller ion than that of oxygen and as such might reduce the stress in the scale.

## Effect of Ion Size

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As suggested in reference 2, the ion size of the metal ion in the oxide appears to be the controlling factor in determining whether an addition will be beneficial in retarding the oxidation of niobium, at least at lower alloying-element content (fig. 2). Appreciable solid solubility in ionic crystals does not occur unless the ion sizes do not differ by more than 15 percent and the ions have similar valences (ref. 13). The ion size of the  $\text{Nb}^{+5}$  ion is 0.70 angstrom (ref. 14). While the sizes of ions dissolved in  $\text{Nb}_2\text{O}_5$  are not known exactly, it is apparent (table V) that all of the elements that offer protection have ions whose size permits them to dissolve into the  $\text{Nb}_2\text{O}_5$  lattice. This solution of smaller ions would tend to reduce the P-B ratio, resulting in less compressive stress in the growing bulk scale, which would in turn reduce the cracks in the scale that lead to porosity. The  $\text{Al}^{+3}$  ion, which is very small compared with the other protective addition elements, would tend to form a second phase, probably  $\text{Al}_2\text{O}_3$ , as it dissolves in the oxide lattice. This second phase, because of its different expansion properties compared with the  $\text{Nb}_2\text{O}_5$ , would tend to distort the lattice. This distortion in addition to thermal stresses upon cooling may account for the powdery texture of the scale with increased Al content. (Several d-values that might be interpreted as  $\text{Al}_2\text{O}_3$  lines were found, see table V.) The  $\text{Ti}^{+4}$  ion is slightly smaller than the  $\text{Nb}^{+5}$  ion and should be quite soluble in  $\text{Nb}_2\text{O}_5$ . Titanium additions were among the best in conferring protection. A similar situation exists with chromium. On the other hand, elements having very small ionic radii, such as boron, silicon, and others (see table VI), or those having very large ionic radii, such as thorium, hafnium, and others, cannot be expected to be appreciably soluble in  $\text{Nb}_2\text{O}_5$  in a substitutional manner without drastically altering the normal  $\text{Nb}_2\text{O}_5$  structure. The results indicate these elements are not helpful in retarding the rate of oxidation of niobium.

The only exception to the solubility relation discussed is the  $\text{Zr}^{+4}$  ion, which does confer protection. However, enough of these  $\text{Zr}^{+4}$  ions are required to be present in the scale to form a second oxide phase. As stated previously, in moderate concentrations this element tends to form a complex oxide ( $6\text{ZrO}_2 \cdot \text{Nb}_2\text{O}_5$ ).

Recent investigations (refs. 11 and 15) came to much the same conclusions regarding the importance of ion size.

## Effect of Sintering and Oxide Plasticity

Other factors that are very important but not well understood are the sintering and plasticity of the scale at the oxidation temperature. There is a much smaller increase in the scaling rate between 1000° and 1200° C than was originally anticipated for such elements as titanium. The glazed appearance of these scales suggests that this might be attributed to the increased protection offered by a sintered, more dense scale with the possibility of crack healing. These effects might be due to the fact that at these temperatures the scale is more plastic and better able to accommodate to the bulk metal, so that cracking is reduced. As mentioned previously, the platinum-group metals as a fine, inert dispersion in Nb<sub>2</sub>O<sub>5</sub> tend to protect by introducing a ductile metallic second phase in the oxide.

## SUMMARY OF RESULTS

This investigation concludes a study to determine the effects of up to 25 atomic percent of 33 alloying additions, prepared by powder-metallurgy techniques, on the oxidation characteristics of niobium. The alloying elements were selected on the basis of existing oxidation theory and to give a reasonably complete coverage of the periodic table. The alloys were evaluated by oxidizing in an air atmosphere for 4 hours at 1000° C and 2 hours at 1200° C. The following results were obtained:

1. Titanium and chromium improved oxidation resistance at both evaluation conditions. However, a more detailed study on the niobium-chromium system (ref. 3) showed that it conferred little protection at 1200° C.

2. Vanadium up to 10 atomic percent at 1000° C improved oxidation resistance even though the scale tended to liquefy, and aluminum up to 10 atomic percent was beneficial at 1000° C even though the specimens became brittle and the scale powdery. Five-atomic-percent cobalt, copper, and iron, and 25-atomic-percent iridium improved oxidation resistance at 1200° C. Results of other investigations for tungsten and molybdenum, though somewhat contradictory, indicate that tungsten up to about 10 atomic percent is protective up to about 1000° C (refs. 4 to 6), while molybdenum up to about 5 atomic percent is protective in the same temperature range (refs. 4 and 5). Reference 4 states that 20-atomic-percent tantalum is protective at 1100° C.

3. The most important factor influencing the rate of oxidation was the ion size of the alloy additions. Ions slightly smaller than the Nb<sup>+5</sup> ion are soluble in the oxide lattice and tend to lower the compressive



stresses in the bulk scale that lead to cracking. This solubility also depends on valence to some extent. All of the elements in items 1 and 2 tend to fit this criterion with the possible exception of aluminum, whose extremely small size would, when in large concentrations, probably lead to the formation of a powdery scale. Maintenance of a crack-free bulk scale for as long as possible may contribute to the formation of a dark subscale, which ultimately is rate-controlling in the oxidation process.

4. The platinum-group metals, especially iridium, appear to protect by entrapment of the alloying element by the incoming  $\text{Nb}_2\text{O}_5$  metal-oxide interface. This inert metallic iridium, when alloyed in sufficient amounts with niobium, appears to give a ductile phase dispersed in the brittle oxide. This scale would then flow more easily to relieve the large compressive stresses. The stresses are introduced from the large oxide to metal volume ratio that tends to crack the oxide.

5. It has been shown that complex oxide formation (which both Ti and Zr tend to initiate) and valence effects, which probably change the vacancy concentration in the scale, are masked by the overriding tendency for a porous scale.

None of the binary alloys improved the oxidation resistance of niobium sufficiently for widespread use in an air atmosphere. It appears evident that additional alloying beyond binary alloys will be required. Such alloys are being reported (refs. 11 and 16); however, it is believed that further improvements are required. Such improvements are likely through broad surveys (of the type reported herein) applied to more complicated systems and, more important, through detailed studies of the mechanism of oxidation.

During this investigation several fundamental areas that appear to need further study became evident: Studies to determine (1) the nature, formation, and stability of subscale, (2) whether a proper combination of alloy additions can reduce the compressive stresses (i.e., Pilling-Bedworth ratio) to a reasonable level essentially to eliminate porosity or increase the plasticity of the oxide, and (3) whether special oxides such as complex niobates or spinels must be formed before true protection begins.

Lewis Research Center  
National Aeronautics and Space Administration  
Cleveland, Ohio, August 2, 1960

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TABLE I. - PURITY, MESH SIZE, AND SOURCE OF ALLOYING POWDERS

Element	Purity, percent	Mesh size	Source
Boron	99.5	-325	Cooper Metallurgical Associates
Aluminum	99+	-200	Charles Hardy, Inc.
Silicon	97	-325	Charles Hardy, Inc.
Calcium	99.5	3/8x80	Var-Lac-Oid Chemical Co.
Scandium	99.9	-325	Var-Lac-Oid Chemical Co.
Titanium (TiH)	99+	-300	Charles Hardy, Inc.
Vanadium	99.7	-20	Var-Lac-Oid Chemical Co.
Chromium	99.5	-325	Charles Hardy, Inc.
Manganese	97.0	-325	Metals Disintegrating Co.
Iron	98.5	-325	Charles Hardy, Inc.
Cobalt	97.73	-300	Charles Hardy, Inc.
Nickel	99+	-300	Charles Hardy, Inc.
Copper	99+	-325	Charles Hardy, Inc.
Germanium	99.99	-100 + 200	Var-Lac-Oid Chemical Co.
Selenium	99.5	-200	A. D. Mackay, Inc.
Zirconium (ZrH)	99	-325	Metals Disintegrating Co.
Molybdenum	99.9	-325	Fansteel Metallurgical Corp.
Ruthenium	99.5	-100 + 200	Var-Lac-Oid Chemical Co.
Rhodium	99.5	-80	A. D. Mackay, Inc.
Palladium	99.5	-80	A. D. Mackay, Inc.
Tin	99.5	-325	A. D. Mackay, Inc.
Antimony	99.5	-325	A. D. Mackay, Inc.
Praseodymium	From 99% oxide	-50	Var-Lac-Oid Chemical Co.
Neodymium	From 99.5% oxide	-50	Var-Lac-Oid Chemical Co.
Hafnium	99	-100	A. D. Mackay, Inc.
Tantalum	99.7	-325	Fansteel Metallurgical Corp.
Tungsten	99.9	-200	Charles Hardy, Inc.
Rhenium	99.9	-200	A. D. Mackay, Inc.
Osmium	99.5	-80	A. D. Mackay, Inc.
Iridium	99.5	-100 + 200	Var-Lac-Oid Chemical Co.
Platinum	99.5	-80	A. D. Mackay, Inc.
Lead	99.0	-325	A. D. Mackay, Inc.
Thorium	99.0	-100	A. D. Mackay, Inc.

TABLE II. - SINTERING CONDITIONS

Element	Atomic number	First sinter			Second sinter		
		Temperature, °F	Time, hr	Atmosphere	Temperature, °F	Time, hr	Atmosphere
B	5	2000	7.5	Vacuum	3100	1/2	Argon
Al	13	1500	1/2		3100	1/2	Vacuum
Si	14	2400	1/2		3300	1/2	
Ca	20	1000	40		1000	40	
Sc	21	2000	6.5		2400	1/2	
Ti	22	3100	1/2		3500	1/2	
V	23	3100	1/2		3500	1/2	
Cr	24	3100	1/2		3500	1/2	↓
Mn	25	2000	7.5		3100	1/2	Argon
Fe	26	2600	1/2		3100	1/2	Vacuum
Co	27	2500	1/2		3100	1/2	↓
Ni	28	2600	1/2		3100	1/2	
Cu	29	1900	1/2		3100	1/2	↓
Ge	32	1700	7.5		3100	1/2	Argon
Se	34	(a)					
Zr	40	3000	1/2		3500	1/2	Vacuum
Mo	42	3100	1/2		3500	1/2	↓
Ru	44	2850	1/2		2850	1/2	
Rh	45	2400	1/2		2400	1/2	
Pd	46	2600	1/2		2600	1/2	
Sn	50	600	40		600	40	
Sb	51	1000	40		1000	40	↓
Pr	59	1500	8		2850	1/2	Argon
Nd	60	1500	8		2850	1/2	Argon
Hf	72	3100	1/2		3500	1/2	Vacuum
Ta	73	3100	1/2		3500	1/2	↓
W	74	3100	1/2		3500	1/2	
Re	75	3100	1/2	↓	3500	1/2	
Os	76	3100	1/2	Argon	3100	1/2	
Ir	77	3100	1/2	Vacuum	3500	1/2	↓
Pt	78	2850	1/2	Vacuum	2500	1/2	Argon
Pb	82	600	40	Argon	600	40	Vacuum
Th	90	2850	1/2	Argon	2850	1/2	Argon

<sup>a</sup>First sinter: 300° → 600° → 800° → 1000° F, 1/2 hr each vacuum.

Re-press: 1000° → 1500° → 2000° F, 1/2 hr each vacuum.

Re-press: 2000° → 2500° → 3000° F, 1/2 hr each vacuum.

2000° → 2500° → 3000° F, 1/2 hr each vacuum (repeat sinter).

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[illegible][illegible]

TABLE IV. - CHEMICAL ANALYSES OF VARIOUS NIOBIUM ALLOY SCALES

Alloy (nominal at. %)	Temper- ature, °C	Oxide class	Niobium, percent by weight	Additive, percent by weight	Color
25 Ti	1000	1	66.4	8.04	White
25 Ti	1200	1	87.2-92.9	4.82-8.94	Tan
1 Al	1000	1	78.87	.08	White
10 Al	↓	2	63.5	7.99	White
1 Cr		1		.76	Green
2 Cr		1		.18	↓
5 Cr		1		<sup>a</sup> .39	
5 Cr (2)		1		<sup>a</sup> 2.58	
17 Cr		2	70.93	1.59	
1 Cr	1200	1		.10	
1 Re	1200	1		<sup>b</sup> .41	Red-purple
5 Co	1000	3	60.7	.99	Brown
5 Co	1200	1	55.55	1.12	Brown-purple
5 Mo	1000	3	68.6	3.49	Purple
25 Ir	1200	1	46.27	36.2	Black
5 V	1000	1	67.72	1.94	Pink
10 V	1000	1	65.3	4.42	Pink
5 Fe	1000	2	63.5	1.78	Dark green
5 Fe	1200	1	71.71	1.18	Dark green
5 Cu	1200	1	68.8	~1.0	Mustard brown
25 Ta	1000	5	44.7	32.8	White
25 Zr	1000	5	62.4	11.1	White

<sup>a</sup>The oxide containing 0.39 percent Cr was gray-green, and a second specimen containing 2.58 percent Cr was a darker green.

<sup>b</sup>Some Re oxide vaporized.



TABLE V. - X-RAY d-VALUES FOR VARIOUS ALLOY SCALES (SCALED AT 1000° C)

H•Nb <sub>2</sub> O <sub>5</sub>		Scale type																
Inovar	Ref. 3	1	1	1	3	1	1	1	2	3	1	4	2	1	2	5	5	1
		Nominal composition of alloying elements																
		1% Al	2% Al	2% Cr	5% Co	5% Cr (1)	5% Cr (2)	5% Fe	5% Mo	5% V	5% Zr	10% Al	10% V	17% Cr	25% Zr	25% Ta	25% Ti	
5.14			5.12											7.51			6.04	
4.67																	5.56	
																	5.15	
3.75	3.72	3.73	3.72	3.73	3.74	3.75	3.74		3.74	3.74	3.73	3.73	3.72	3.74		3.89	3.72	
3.65	3.63	3.62	3.63	3.63	3.58	3.57	3.63	3.57	3.62	3.63	3.63	3.57		3.62		3.72	3.72	
			3.56											3.57		3.63	3.55	
3.49	3.48	3.48	3.48	3.48	3.51		3.49		3.51	3.48	3.49	3.43	3.52	3.48	3.54	3.46	3.41	
3.36	3.34	3.34	3.34	3.35			3.34	3.43	3.35	3.35			3.36	3.34				
3.16																3.13		
																3.07		
2.83	2.82	2.82	2.82	2.83		2.78	2.83		2.84	2.83	2.82		2.88	2.82	2.95		2.77	
2.78	2.76	2.70	2.76				2.70	2.78	2.77	2.70		2.78		2.77			2.68	
2.71	2.54	2.54	2.53	2.69			2.54		2.52	2.54	2.53			2.70				
	2.49		2.48										2.48			2.45		
																2.41		
	2.25	2.31	2.44	2.31		2.31	2.31	2.31	2.31	2.31	2.32	2.31	2.31	2.31	2.31		2.30	
	2.07	2.07	2.07		2.06		2.07		2.07	2.06			2.06					
	2.03	2.04	2.04			2.05	2.04	2.04	2.04		2.05	2.05		2.05	2.05		2.05	
	1.91	1.90	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.91	1.90		1.90	
	1.78		1.79				1.74	1.74					1.73	1.78		1.79	1.78	
	1.68	1.68	1.68	1.68	1.68	1.68	1.68	1.68	1.68	1.68	1.68	1.68	1.68	1.68	1.67	1.66	1.67	
																	1.66	
	1.58	1.58	1.58	1.58	1.58	1.57	1.58	1.57	1.58	1.58	1.58	1.57	1.58	1.58	1.58		1.62	
	1.55								1.56	1.55	1.55						1.57	
									1.46					1.45				
									1.40	1.40	1.40	1.40	1.40	1.40	1.40			
									1.39									
	1.30	1.30	1.28						1.28			1.30					1.39	
	1.28								1.27									

H. Inouye, "The Sealing of Columbium in Air." Speech before AIME Reactive Metal Conference, Buffalo, New York, Mar. 19-21, 1956.

TABLE VI. - X-RAY d-VALUES FOR VARIOUS SCALES (SCALED AT 1200° C)

H·Nb <sub>2</sub> O <sub>5</sub> (Inouye)	Scale type							
	4	1	1	3	1	1	1	1
	Nominal composition of alloying elements							
	1% Al	1% Cr	1% Re	5% Cr	5% Cu	5% Fe	25% Ir	25% Ti
5.11	5.11	5.10	5.09	5.04		5.16		
4.60		4.61				4.78	4.41	
		4.38				4.01		
3.72	3.73	3.73	3.76	3.73	3.73	3.73	3.72	3.72
3.63	3.63	3.63	3.63	3.62	3.63	3.58	3.63	3.56
3.48	3.48	3.48	3.49	3.47	3.47	3.48	3.48	3.42
3.34		3.34		3.34	3.33	3.43		
3.15				2.88	3.14			
2.82	2.83	2.82	2.83	2.82	2.82	2.83	2.82	
2.77	2.76	2.76	2.77	2.79	2.76	2.78		2.77
2.70	2.70	2.70	2.71	2.70	2.70	2.70		
(1000° C) 2.54	2.54	2.54	2.55		2.54	2.54		2.54
(1000° C) 2.49		2.48			2.48			2.39
	2.31	2.31	2.32	2.31	2.30	2.31	2.21	2.30
	2.07	2.07	2.08	2.07	2.07			
	2.03	2.03	2.04		2.03	2.04		2.05
	1.91	1.91	1.91	1.91	1.91	1.91	1.92	1.90
		1.82	1.82		1.82			
		1.78			1.78	1.78		
	1.74	1.74	1.74		1.74			
	1.69	1.68	1.68	1.68	1.68	1.68	1.68	1.67
								1.64
	1.58	1.58	1.58	1.58	1.58	1.58		
		1.55	1.56	1.55	1.55			
		1.45		1.45				
		1.41	1.41	1.40	1.40	1.40		
		1.39	1.39		1.39			1.39
							1.35	
		1.28	1.28	1.28				
		1.26						

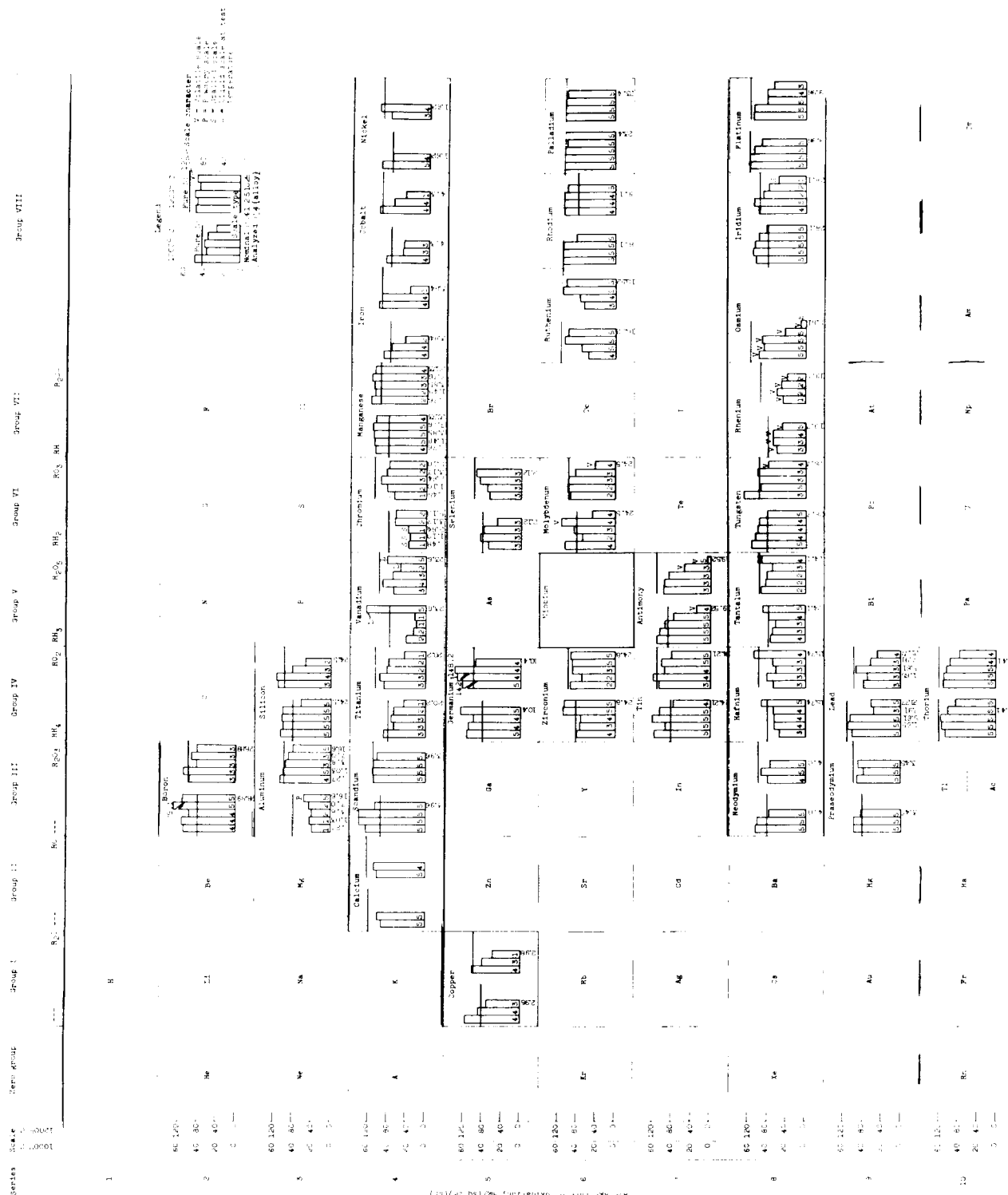


Figure 1. - Summary of air-oxidation tests on sintered niobium binary alloys.

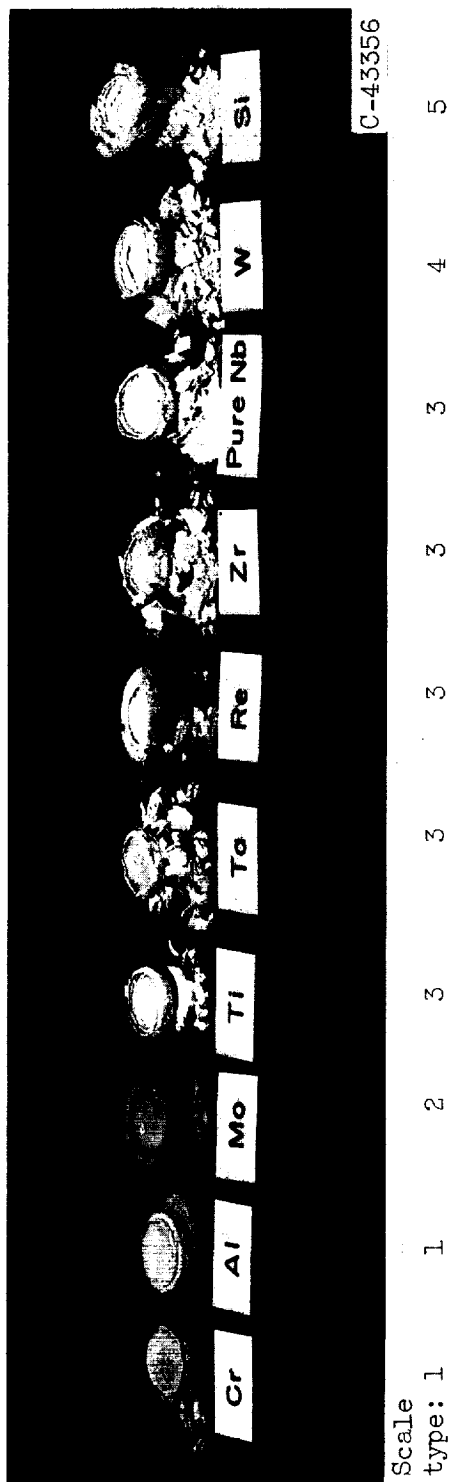
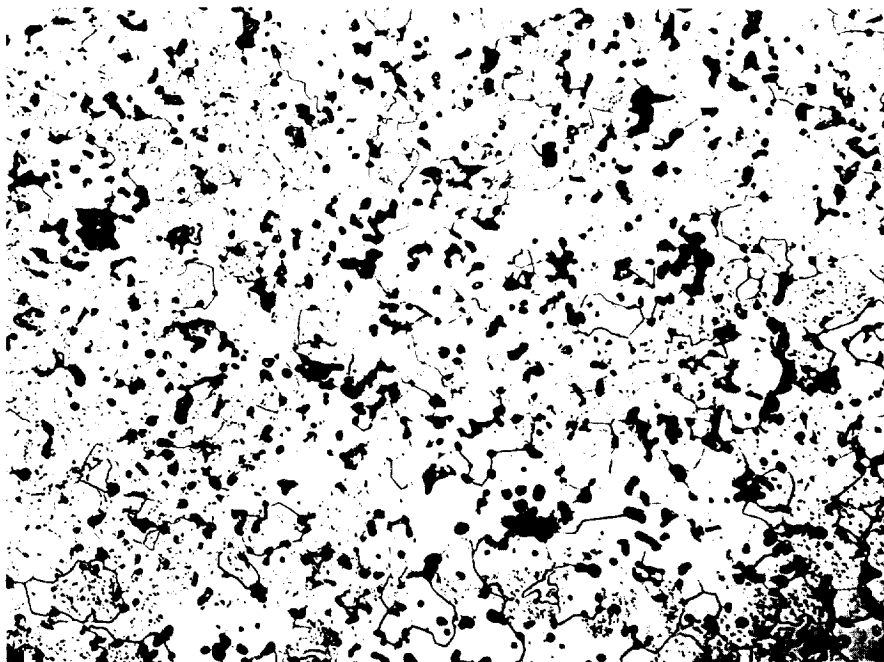
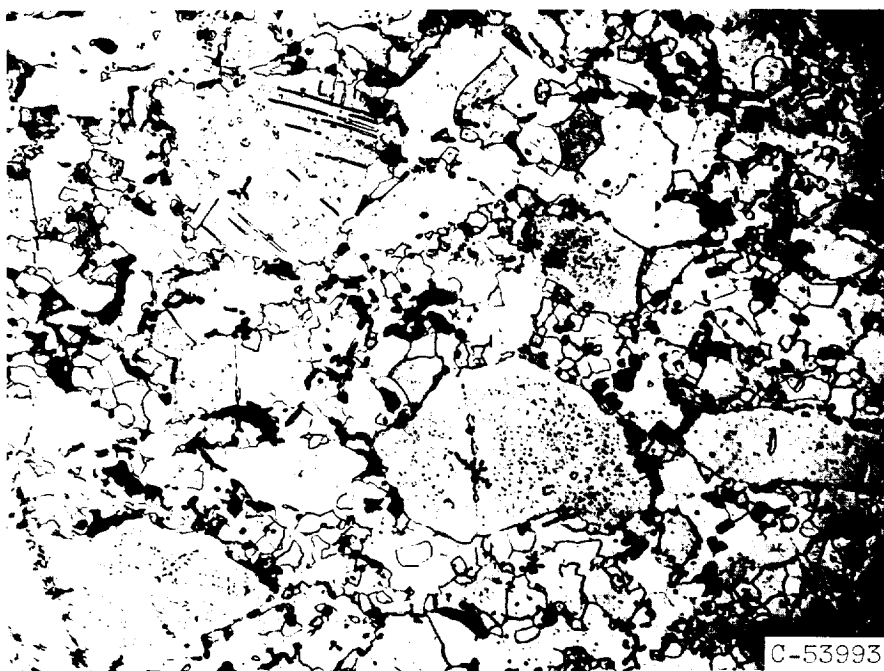


Figure 2. - Effect of 2-atomic-percent (nominal) alloy on oxidation of niobium; test for 4 hours in air at 10000 C.



(a) Niobium - 2 percent vanadium alloy.



(b) Niobium - 1 percent cobalt alloy.

Figure 3. - Two typical sintered niobium alloys. Etchant: 10  $\text{HNO}_3$ , 10  $\text{H}_2\text{O}$ , and a few drops of  $\text{HF}$ . X250.



<p>NASA TN D-283 National Aeronautics and Space Administration. OXIDATION BEHAVIOR OF BINARY NIOBIUM ALLOYS. Charles A. Barrett and James L. Corey. November 1960. 27p. OTS price, \$0.75. (NASA TECHNICAL NOTE D-283)</p> <p>This report completes a screening study on the oxidation resistance of 33 binary alloy systems of niobium. Alloys containing up to 25 nominal atomic percent of the alloying element were prepared by powder-metallurgy techniques and oxidized in air for 4 hours at 1000° C and 2 hours at 1200° C. The alloy systems showing the best oxidation resistance were Nb-Cr, Nb-Ti, Nb-Al, Nb-V, and to a lesser extent Nb-Fe, Nb-Co, Nb-Cu, and Nb-Ir. The chief factor contributing to this protection appears to be the ion size of the alloy addition. It should be slightly smaller than that of the Nb<sup>+5</sup> ion, in order to dissolve in the Nb<sub>2</sub>O<sub>5</sub> oxide and lower the compressive stresses that crack the scale.</p> <p>Copies obtainable from NASA, Washington</p>	<p>I. Barrett, Charles A. II. Corey, James L. III. NASA TN D-283</p> <p>(Initial NASA distribution: 13, Chemistry, inorganic; 26, Materials, other.)</p> <p>NASA</p>	<p>NASA TN D-283 National Aeronautics and Space Administration. OXIDATION BEHAVIOR OF BINARY NIOBIUM ALLOYS. Charles A. Barrett and James L. Corey. November 1960. 27p. OTS price, \$0.75. (NASA TECHNICAL NOTE D-283)</p> <p>This report completes a screening study on the oxidation resistance of 33 binary alloy systems of niobium. Alloys containing up to 25 nominal atomic percent of the alloying element were prepared by powder-metallurgy techniques and oxidized in air for 4 hours at 1000° C and 2 hours at 1200° C. The alloy systems showing the best oxidation resistance were Nb-Cr, Nb-Ti, Nb-Al, Nb-V, and to a lesser extent Nb-Fe, Nb-Co, Nb-Cu, and Nb-Ir. The chief factor contributing to this protection appears to be the ion size of the alloy addition. It should be slightly smaller than that of the Nb<sup>+5</sup> ion, in order to dissolve in the Nb<sub>2</sub>O<sub>5</sub> oxide and lower the compressive stresses that crack the scale.</p> <p>Copies obtainable from NASA, Washington</p>	<p>I. Barrett, Charles A. II. Corey, James L. III. NASA TN D-283</p> <p>(Initial NASA distribution: 13, Chemistry, inorganic; 26, Materials, other.)</p> <p>NASA</p>
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